Filling the Gap in Plutonium Properties

Studies at Intermediate Temperatures and Pressures

Albert Migliori, Alan J. Hurd, Yusheng Zhao, and Cristian Pantea

Pure plutonium exhibits unusual sensitivity to processing, impurities, and aging because its *f*-electrons straddle the boundary between bonding and localization, and plutonium-gallium alloys are unstable to changes in pressure and temperature. Small thermodynamic perturbations, self-irradiation, ingrowth of radiogenic elements, and aging destabilize most plutonium behaviors, while the many structural phases occur within a narrow range of pressures and temperatures (within a few gigapascals and a few hundred kelvins of ambient temperature). This sensitivity and complexity of plutonium and plutonium-gallium alloys make it difficult to obtain reliable measures of the important equation of state (EOS), which describes the relationship among density, temperature, and pressure in a material and therefore serves as input to hydrodynamic calculations. Although an actual full implosion is the most sensitive test of the EOS, such a test benefits enormously if performed on accurately characterized starting materials. It is clear, therefore, that one of our essential functions at the Laboratory is to use the highest-fidelity measurements available to establish the EOS as far up the pressure-temperature (*P-T*) curve as we can manage.

Satisfying this urgent need will support the development of property/performance models, ab initio atomistic computation, Kolski bar and light-gas-gun studies, hydrotests, and more, all of which are aimed at better understanding the connections among aging, physical properties, and weapon performance. Better, more-comprehensive, more-accurate static measurements of plutonium at higher temperatures and pressures than now available can also improve our estimation of margins and uncertainties when applied to new or old computations.

Where Does LANSCE Come in?

The tricky part of any attempt to push static measurements beyond ambient temperature and pressure is that plutonium has two "volumes." One is a measure of the exact distance between atoms—the crystallographic unit cell. This volume is determined by the most fundamental physics of plutonium and its alloys, and it equals the volume a chunk of plutonium would have if all the atoms sat on the exact positions determined by the crystal structure. This so-called x-ray volume is measured by diffraction of either neutrons or x-rays. But not all atoms sit where they belong. Many are displaced from their exact positions because of impurities, Frenkel-pair formation (Frenkel pairs are composed of a vacancy in the crystal lattice and the displaced atom), radiation damage, dislocations, interstitials, grain boundaries, and vacancies. And in some regions, such as voids produced by helium ingrowth, there just are not any plutonium atoms. So the second volume is determined by a macroscopic measurement of density, such as weighing the plutonium sample when it is immersed in a fluid.

The difference between these two volumes contains important physics. For example, even in aluminum (Gordon and Granato 2004), a metal with almost none of the complications of plutonium, precise measurements of the difference between these volumes shows a temperature dependence. The dependence occurs because thermal energy can, every once in a while, displace an aluminum atom from its crystallographically correct position, forming a vacancy-interstitial pair. There is a thermal activation energy required for this displacement to happen, and that energy can be found from the difference between the volumes as a function of temperature. In plutonium, we expect the difference to be rich in valuable information and crucial to understanding the way this metal behaves when compressed.

We know how to measure x-ray density at the Los Alamos Neutron Science Center (LANSCE), the Advanced Photon Source (APS) at Argonne National Laboratory, and other facilities where diffraction of x-rays or neutrons is available. However, put plutonium under static pressure, and things get a lot more difficult. X-ray diffraction does not work very well when the low-energy x-rays required have to penetrate the structure of a high-pressure system, so neutron scattering is the technique of choice. But how can one measure the other volume? Radiography is key

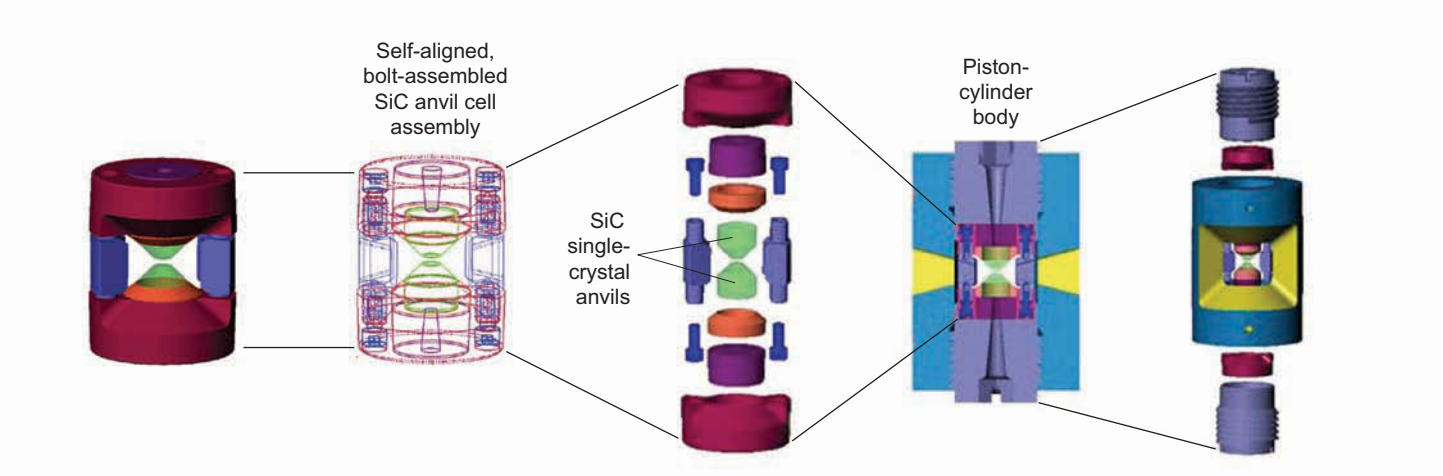

Figure 1. The ZAP Cell, a SiC Anvil Cell Assembly
One of us (Y.Z.) has designed a self-aligning and bolt-turnbuckle cell, which consists of a piston-cylinder body with a SiC (or moissanite) anvil cell assembly at its center (enlarged version is shown at the left of the figure). The SiC cell uses a huge pair of single crystals of SiC, from 5 to 100 carats, to apply pressure on a small sample volume (3~30 mm^3). During a test at the LANSCE HIPPO diffractometer, the SiC cell was loaded to a pressure of 30 GPa in the TAP-98 press, and the whole assembly, including the press, was placed inside the HIPPO chamber. The neutron diffraction signal from small iron samples was strong because of the open structure of the SiC anvil cell assembly and the TAP-98 press. High pressures achieved under high hydraulic loading forces (up to 100 tons) can be locked into the inner cell. Through a unique detachment mechanism, the cell can be removed from the press and can then be easily transported to other experimental setups, where the same sample can be studied under identical pressure-temperature (*P-T*) conditions. The optically transparent windows of SiC anvils are particularly useful for measurement of vibrational spectra (Raman and IR) on the same sample under identical *P-T* conditions. The straightforward anvil-sample-anvil setting allows applications of acoustic transmission and ultrasonic interferometry techniques for elasticity measurements at high pressures.

to the measurement. Using neutron radiography techniques available at LANSCE, we can take a dimensionally accurate picture of samples of plutonium while they are in a high-pressure environment and, at the same time, measure the diffraction density.

Pressure Cell for Simultaneous Measurements of Plutonium Properties

Conventional pressure cells are in place at LANSCE, but the silicon carbide (SiC) anvil cell shown in Figure 1 provides a safe, secure environment and an unusually large working space for the plutonium measurements we want to make. A large plutonium sample (millimeters in size) fits in between the two anvils without touching them and thus leaves enough room for a hydraulic medium to surround it and apply pressure indirectly. Although the pressure in the SiC cell is less than in the conventional diamond cell, inclusion of the hydraulic medium is more important than the higher pressure because no shear stresses or large stress gradients occur in the hydraulic medium and, therefore, the hydrostatic pressure on the sample is accurate and uniform. The stored energy in a SiC cell, as in a diamond anvil cell, is small, and this feature makes any safety issues easy to handle. Large windows in the anvil supports allow neutrons for radiography and diffraction to pass through. Because the large flat SiC anvils themselves are a nearly ideal sound-transmission medium and all the materials involved can withstand temperatures of up to 1800 kelvins and pressures of up to 2 gigapascals, we can conduct the measurements described below.

What Will New Measurements Reveal?

The SiC anvil cell is now operational, and a technique is available to measure the time it takes a sound pulse to traverse a plutonium sample under pressure. The speed of sound in plutonium is a direct measure of the metal's elastic stiffness, and from it the bulk modulus can be derived. The bulk modulus of plutonium gives a measure of its compressibility, and it is the very first quantity theorists compute from an electronic-structure model. It is also, therefore, one of the most important material properties for validating any ab initio or molecular-dynamic model of plutonium. Measurements of bulk modulus in a SiC anvil cell require a technique called pulse-echo ultrasound, an old and widely applied method. But to get the precision we need to see very

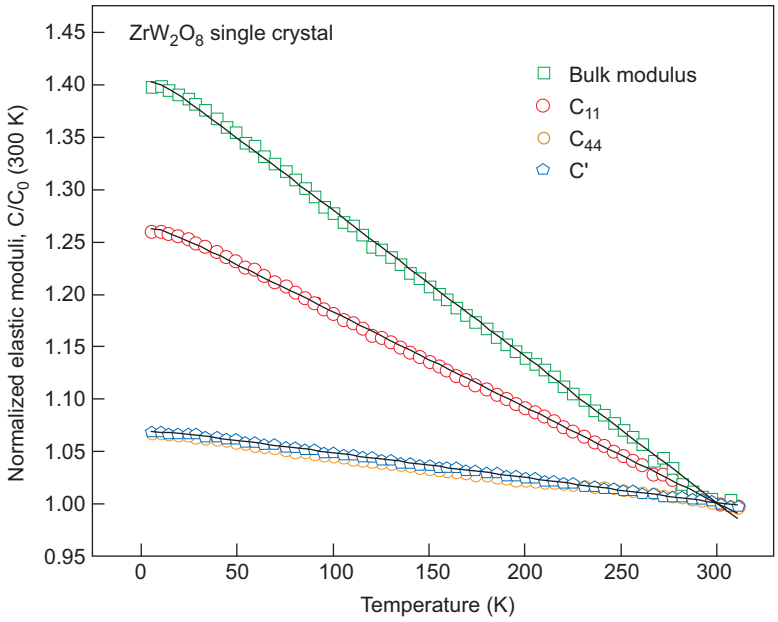

Figure 2. Elastic Moduli of Zirconium Tungstate vs Temperature
For zirconium tungstate, the softening on warming would be ordinary if it were not for the fact that this material contracts as it warms, and contracting solids usually stiffen.

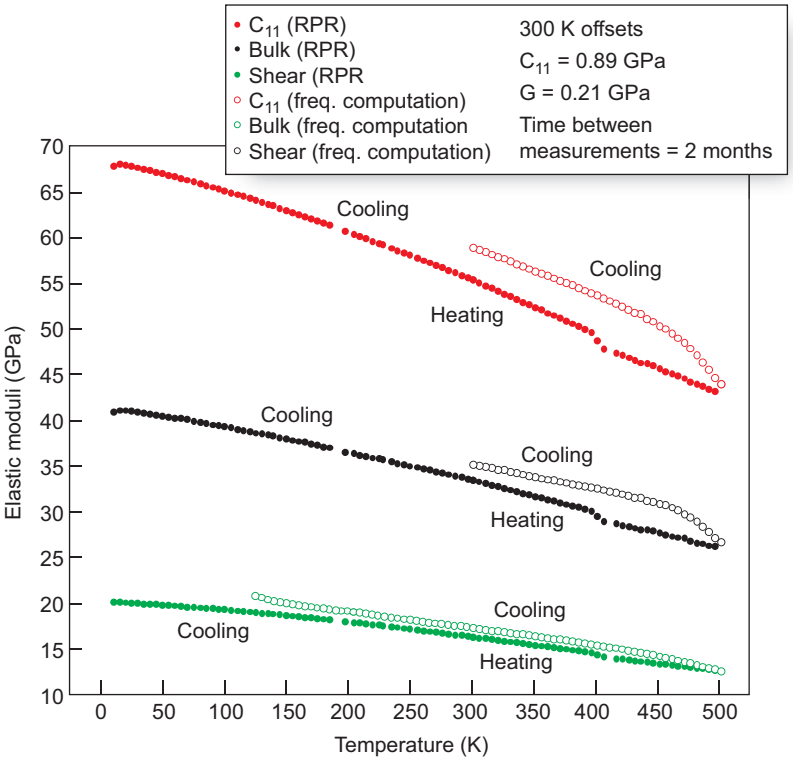

Figure 3. Elastic Moduli of a Plutonium-Gallium Alloy vs Temperature
One can observe a pronounced softening of the plutonium-gallium alloy above 350 K, where this material, like zirconium tungstate, contracts on warming. A natural prediction is that it must also soften when compressed, a phenomenon not recorded in any of the plutonium databases.

small changes with age, strain, and other parameters, we developed an all-digital signal-processing ultrasound system that enables time-of-flight determination to parts per million, while the sample is hot and compressed. Of course, to get the speed of sound (and bulk modulus), we need not only the time of flight of the sound pulse, but the length of the sample. Here is where radiography and diffraction come in. Using the SiC anvil cell to apply pressure at elevated temperature, radiography to measure length changes, and hence volume, pulse-echo ultrasound to measure time of flight, and neutron diffraction to measure unit-cell volume and structure, we have a tremendously powerful, complete tool, which permits many of the measurements to be done simultaneously. The combination yields both immersion volume and unit-cell volume versus pressure and temperature, basically the two equations of state. Also determined are the thermal expansion coefficient and the bulk modulus (and shear modulus) versus temperature. Within the working envelope of this system, we can also access the liquid state. The liquid phase of metals helps understand shocked metals. Unresolved discrepancies between melting curves derived from shock measurements and those from static experiments have been documented (Luo et al. 2003a, Luo et al. 2003b). Understanding melting and melt structure is fundamental to a material's behavior along a shock Hugoniot. Moreover, the study of high-pressure melting is of interest for density-functional theory and molecular dynamics, which can be incorporated into dynamic simulations of shock.

Implication of New Measurements

If we can implement this set of measurements, we expect to provide

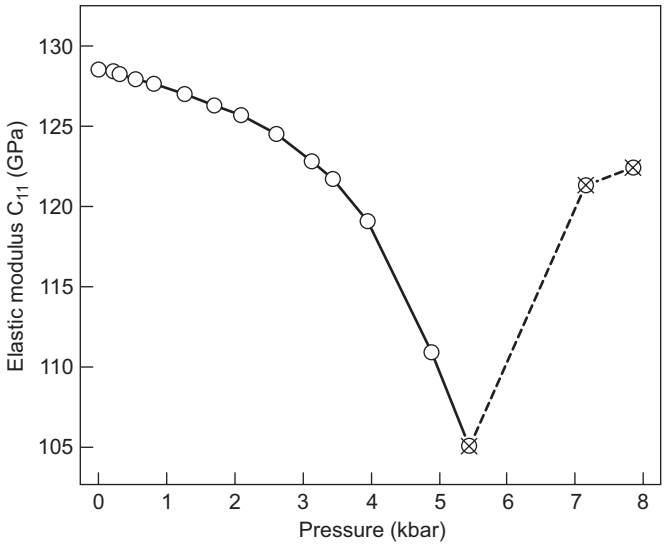

Figure 4. Elastic Moduli of Zirconium Tungstate vs Pressure
We obtained the elastic moduli of zirconium tungstate as we compressed the material. Unlike most solids, this material softens under pressures of up to about 0.5 GPa.

state-of-the-art accuracy of the plutonium EOS over a range of temperatures and pressures heretofore largely ignored at this level of precision. We should also be able to validate extrapolation of aging effects at higher pressures and watch aging in real time at elevated temperatures and pressures. But perhaps there will be some surprises, as well as expansion of the database.

For example, both δ-plutonium (above 375 kelvins) and a zirconium tungstate (ZrW_2O_8) have negative thermal expansion (Figure 2). For plutonium, Angus Lawson has proposed an "invar" model, in which two phases—one is a high-temperature, low-volume phase—are simultaneously present. As temperature changes, more of the low-volume phase appears. Although both phases can have perfectly ordinary properties, the mixture can compensate ordinary thermal expansion, leaving a material that shrinks when heated, and the model works well for plutonium-gallium alloys. But the elastic response of plutonium-gallium is much stranger. We have shown (Drymiotis et al. 2004, Migliori et al. 1993) that both ZrW_2O_8 and plutonium-gallium soften upon warming in regions where the thermal expansion coefficient is negative (refer to Figures 2 and 3). How can a material get softer as volume decreases? Most conventional models predict that, as a material is compressed and its density increases, it should get stiffer and harder to compress. An even bigger surprise, measured using the SiC anvil cell and the pulse-echo ultrasound system described here, is that ZrW_2O_8 softens when compressed at constant temperature (Figure 4). Can the invar model account for this phenomenon and encompass more than just plutonium, or are other models better at accounting for it? An example would be the Simon-Varma constrained-lattice model (Simon and Varma 2001). What does plutonium-gallium do during the first 2 gigapascals or so of compression at constant temperature? We do not know. If plutonium-gallium also softens, this will be an important new result. We now have the tools for the measurements and plan to find the answer. ■

Further Reading

Drymiotis, F. R., H. Ledbetter, J. B. Betts, T. Kimura, J. C. Lashley, A. Migliori, et al. 2004. Monocrystal Elastic Constants of the Negative-Thermal-Expansion Compound Zirconium Tungstate (ZrW_2O_8). *Phy. Rev. Lett.* **93** (2): 025502.

Gordon, C. A., and A. V. Granato. 2004. Equilibrium Concentration of Interstitials in Aluminum Just Below the Melting Temperature. *Mater. Sci. Engin. A* **370** (1–2): 83.

Hixson, R. S., D. A. Boness, J. W. Shaner, and J. A. Moriarty. 1989. Acoustic Velocities and Phase Transitions in Molybdenum under Strong Shock Compression. *Phys. Rev. Lett.* **62** (6): 637.

Luo, S.-N., T. J. Ahrens, and P. D. Asimow. 2003a. Polymorphism, Superheating, and Amorphization of Silica Upon Shock Wave Loading and Release. *J. Geophys. Res.–Solid Earth* **108** (B9): 2421.

Luo, S.-N., T. J. Ahrens, T. Cagin, A. Strachan, W. A. Goddard III, and D. C. Swift. 2003b. Maximum Superheating and Undercooling: Systematics, Molecular Dynamics Simulations, and Dynamic Experiments. *Phys. Rev. B* **68**: 134206.

Migliori, A., J. L. Sarrao, W. M. Visscher, T. M. Bell, M. Lei, Z. Fisk, and R. G. Leisure. 1993. Resonant Ultrasound Spectroscopic Techniques for Measurement of The Elastic Moduli of Solids. *Physica B* **183** (1–2): 1.

Migliori, A., and J. L. Sarrao. 1997. *Resonant Ultrasound Spectroscopy*: *Applications to Physics*, *Materials Measurements*, *and Nondestructive Evaluation*. New York: Wiley.

Shaner, J. W. 1988. Grüneisen Gamma and Acoustic Velocity for Soft Sphere Fluids. *J. Chem. Phys.* **89** (3):1616.

Simon, M. E., and C. M. Varma. 2001. Dynamics of Some Constrained Lattices. *Phys. Rev. Lett.* **86** (9): 1781.

Zhao, Y., D. He, J. Qian, C. Pantea, K. A. Lokshin, J. Zhang, and L. L. Daemen. 2005. Development of High P-T Neutron Diffraction at LANSCE. In Advances in High-Pressure Technology for Geophysical Applications. Chapter 23, p. 461. Edited by J. Chen, Y. Wang, T. S. Duffy, G. Shen, and L. P. Dobrzhinetskaya. Oxford, UK: Elsevier.